PREPARATION AND PROPERTIES OF THE ALKALI AND ALKALINE EARTH METAL PERCHLORATE AMMINES

BY

EDWIN GEORGE KOCH

A. B., University of Montana, 1928

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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INTRODUCTION

Although the chemical literature on the subject of ammino-metallic salts is extensive, the ammines of metallic perchlorates have been comparatively little investigated. Roscoe in 1863 described the preparation of tetrammino-cupric perchlorate. At that time very few ammines of any type had been prepared. In 1912 the study of perchlorate ammines was resumed by Salvadori. This study included the ammino-perchlorates of cobalt, nickel, manganese, cadmium, zinc, and copper. Six years later Ephraim described the preparation of two ammino-auric perchlorate salts and one ammino-lithium perchlorate. Nothing more appeared until Line, in 1928, made a rather extensive study of the ammines of magnesium perchlorate.

During the past thirty years Bonnefoi, Salvadori, Ephraim, Biltz and Hüttig, Biltz, Hüttig, Clark, and a few others have made extensive studies of the ammino-metallic compounds, dealing mainly with metallic halides, and not at all with metallic perchlorates.

This investigation was undertaken with the object of preparing the ammino-perchlorates of magnesium, calcium, strontium and barium, of studying their chemical and physical properties, and of comparing them with the amino-halides of the same metals found in the literature. The investigation includes the preparation of ten ammines, determination of their composition, their densities from which molecular volumes are calculated, qualitative and semi-quantitative study of certain properties, and thermal studies.

EXPERIMENTAL

Working at room temperature and above, the stable ammino-perchlorates of magnesium, calcium, strontium, and barium were prepared by one or more of the following methods: (1) by passing dry ammonia gas over a sample of the anhydrous perchlorate at room temperature to constant weight; (2) by passing dry ammonia gas into a chamber containing the anhydrous perchlorate at a predetermined pressure and temperature (obtained from a study of temperature-pressure equilibria) to constant weight; (3) by means of equilibria established in a vacuum

desiccator between (a) excess anhydrous perchlorate in the presence of a weighed sample of the hexammine, and (b) excess of the hexammino-perchlorate in the presence of a weighed sample of the anhydrous salt; (4) by isothermal decomposition of the higher to the lower ammines at suitable temperatures. The ammines were prepared from analysed samples of anhydrous material, and were analysed for ammonia content after preparation.

It was found that the anhydrous perchlorates of these metals react vigorously with ammonia gas at room temperature, liberating considerable heat, with the formation of ammines stable at that temperature. As the reaction proceeds, a large increase in volume is noticed. The ammines of these metals are voluminous, white powders. Depending on their vapor pressures at room temperature, they have varying intensities of ammonia odor. All the ammines prepared are very hygroscopic, making a study of them very difficult. All of the ammines formed were found to be soluble to a fair extent in ethyl alcohol, ethyl acetate, and amyl acetate, accompanied by precipitation of hydroxides or basic salts. They are sparingly soluble in ether, forming clear solutions, and are exceedingly soluble in water accompanied by hydrolysis to a slight extent. They are insoluble in toluene, carbon tetrachloride, and benzene. The anhydrous perchlorates dissolve readily in liquid ammonia, accompanied by vigorous reaction, and upon evaporation of ammonia, ammines stable at that temperature are formed. The extent of this solubility, showing the approximate number of mols dissolved in 1000 gms. (58.8 mols) of ammonia, is as follows: $Mg(ClO_4)_2$, 1.7; $Ca(ClO_4)_2$, 2.16; $Sr(ClO_4)_2$, 3.1; $Ba(ClO_4)_2$, 2.0.

Isothermal decompositions were carried out to establish the number and composition of the intermediate stable ammines of the alkaline earth and magnesium metal perchlorates. A form of thermal reaction piezometer was employed. It consisted of a glass tube reaction chamber 40 mm. in diameter and 22 cm. in length, into which the sample in a weighed container could be placed, and equipped with three tubes leading to a closed manometer, a vacuum pump, and to the air. The latter two were equipped with stopcocks. Glass joints were finely ground to produce vacuum tight connections. It was heated by a specially designed vapor-bath oven. Temperature was measured by means of a thermometer suspended in the apparatus. A weighed

sample was placed in the reaction chamber and the apparatus was evacuated. When equilibrium was established, the pressure and temperature were recorded and the sample was then removed, cooled and weighed. This procedure was repeated until equilibrium was established at a lower pressure, indicating a lower, stable form. The compounds shown as a result of these experiments, and verified by other methods of preparation, are as follows: $Mg(NH_3)_2(ClO_4)_2$; $Mg(NH_3)_6ClO_4)_2$; $Ca(NH_3)_2(ClO_4)_2$; $Ca(NH_3)_4(ClO_4)_2$; $Ca(NH_3)_6(ClO_4)_2$; $Sr(NH_3)_2(ClO_4)_2$; $Sr(NH_3)_6(ClO_4)_2$; $Sr(NH_3)_7(ClO_4)_2$; $Ba(NH_3)_2(ClO_4)_2$; $Ba(NH_3)_6(ClO_4)_2$.

Temperature-pressure equilibria were carried out for each ammine listed above, from 0° C. to the temperature at which the pressure reached one atmosphere. As in the case of isothermal decompositions, a form of thermal reaction piezometer was employed, varying in design only slightly from the type described above. The reaction chamber was much smaller, being 15 mm. in diameter and 30 cm. long, and the temperature was determined by means of a thermocouple which dipped into the sample. This apparatus was heated by means of an electric resistance oven. A sample was placed in the apparatus and at various temperatures the equilibrium pressure was noted. The data was graphically plotted. Relative stabilities of the various ammines were determined by taking the temperature in degrees centigrade at which each salt showed a pressure of 100 mm. These values are as follows: $Mg(NH_3)_2(ClO_4)_2$, only 10 mm. at 260°; $Mg(NH_3)_6(ClO_4)_2$, 168°; $Ca(NH_3)_2(ClO_4)_2$, 165° $Ca(NH_3)_4(ClO_4)_2$, 105°; $Ca(NH_3)_6(ClO_4)_2$, 103°; $Sr(NH_3)_2(ClO_4)_2$, 106.5°; $Sr(NH_3)_6(ClO_4)_2$, 58.5°; $Sr(NH_3)_7(ClO_4)_2$, 16.5°; $Ba(NH_3)_2(ClO_4)_2$, 61°; $Ba(NH_3)_6(ClO_4)_2$, 29°. Also from the plotted curves was determined the range of existence of each ammine under one atmosphere of ammonia. They are: $Mg(NH_3)_2(ClO_4)_2$, 227° to the decomposition temperature of the perchlorate radicle (above 250°); $Mg(NH_3)_6(ClO_4)_2$, up to 227°; $Ca(NH_3)_2(ClO_4)_2$, 153°-265°; $Ca(NH_3)_4(ClO_4)_2$, 149-153°; $Ca(NH_3)_6(ClO_4)_2$, up to 149°; $Sr(NH_3)_2(ClO_4)_2$, 104.5°-160°; $Sr(NH_3)_6(ClO_4)_2$, 53°-104.5°; $Sr(NH_3)_7(ClO_4)_2$, up to 53°; $Ba(NH_3)_2(ClO_4)_2$, 74°-112°; $Ba(NH_3)_6(ClO_4)_2$, up to 74°.

Densities of the anhydrous perchlorates and of the various ammines were determined, employing the usual pyknometer

method. The liquids used were carbon tetrachloride and toluene. From the densities were calculated the molecular volumes of the ammines and the apparent volume of ammonia in the coördination sphere. The figures are given for each ammine and for the anhydrous salts, the density appearing first, the molecular volume second, and the volume of ammonia last in each case. $Mg(ClO_4)_2$, 2.60, 85.8; $Mg(NH_3)_2(ClO_4)_2$, 2.053, 125.3, 19.8; $Mg(NH_3)_6(ClO_4)_2$, 1.41, 230.8, 24.2; $Ca(ClO_4)_2$, 2.651, 90.2; $Ca(NH_3)_2(ClO_4)_2$, 2.072, 131.8, 20.8; $Ca(NH_3)_4(ClO_4)_2$, 1.650, 186.1, 23.9; $Ca(NH_3)_8(ClO_4)_2$, 1.442, 236.6, 24.4; $Sr(ClO_4)_2$, 2.973, 96.4; $Sr(NH_3)_2(ClO_4)_2$, 2.403, 133.4, 18.5; $Sr(NH_3)_6(ClO_4)_2$, 1.683, 230.9, 22.4; $Sr(NH_3)_7(ClO_4)_2$, 1.608, 252.4, 22.3; $Ba(ClO_4)_2$, 3.681, 91.4; $Ba(NH_3)_2(ClO_4)_2$, 2.585, 143.3, 25.9; $Ba(NH_3)_6(ClO_4)_2$, 1.898, 231.0, 23.2. The mean value for the volume of ammonia is 22.54 which is in good agreement with values found by Biltz, and Clark, for ammines of other metallic salts.

Several hydrates of the alkaline earth and magnesium metal perchlorates were treated with dry ammonia gas at room temperature. In every instance the water was completely removed from the hydrate, being replaced by ammonia to form the highest stable ammine at that temperature. Experiments of opposite nature were conducted, showing in every instance that atmospheric moisture will replace the ammonia in the ammines. It results that the substance which is in excess (water or ammonia) will replace the other from the coördination sphere, the reaction being reversible.

CONCLUSION

The ammines prepared and studied above were compared with those of magnesium, calcium, strontium, and barium halides appearing in the literature, concerning number and composition of ammines formed, relative stabilities, molecular volumes, and volume of ammonia in the complex. It was found that perchlorate ammines fall between the bromides and iodides in the above respects, there being only a few exceptions.

In recent years Biltz, Ephraim, Clark, and others have reported results of investigations which have dealt to a considerable extent with the attempts to discover and define the various factors influencing the stability of coördination compounds of the

type studied in this paper. In so far as the present investigation is concerned, it is in good agreement with their conclusions. In general, the dimensional influence on stability of coördination compounds is as follows: the stability of ammines increases (1) with decrease in atomic volume of the cation, (2) with decrease in the molecular volume of the neutral molecule, and (3) with increase in ionic volume of the anion. This generalization is not without exceptions. In fact, the exceptions are numerous, but in the case of the hexammines and particularly in compounds with closely related cations and anions it holds well and is a useful guide in the study of these compounds.

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